MTR

Novel Nonporous Fouling-Resistant Composite Nanofiltration Membranes and Membrane Separation Systems for Wastewater Treatment

Second Progress Report

prepared for

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by

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1. INTRODUCTION

This is the second progress report to the Office of Naval Research by Membrane Technology and Research, Inc. (MTR) for Grant No. N00014-96-C-0148, entitled "Novel Nonporous Fouling-Resistant Composite Nanofiltration Membranes and Membrane Separation System for Wastewater Treatment."

Navy ships generate large volumes of wastewater (about 20-70 gal/day of water per crew member), which, to meet new regulations, will require treatment prior to overboard discharge. Such wastewater contains a high level of suspended solids. Treatment by nanofiltration can produce dischargeable water, but all current nanofiltration membranes are finely porous and only moderately hydrophilic. They are, therefore, subject to fouling by particulates, resulting in a dramatic decline in the water flux. Development of fouling-resistant membranes will improve nanofiltration systems by lowering capital costs, reducing energy consumption, and decreasing system down-time.

2. PROGRESS DURING THIS PERIOD

During the period June 15 to August 15 of this project, we prepared nonporous Pebax composite membranes from various grades of commercially available polyamide-polyether block copolymers. Composite membranes were made from Pebax 1074, Pebax 4011, Pebax 3000, Pebax 1041, and Pebax 2533 using our 12-inch wide continuous coating equipment. The gas permeation properties of the composite membranes were tested with nitrogen and carbon dioxide to ensure that the thin Pebax layers were defect-free. The pressure-normalized fluxes of the membranes were determined for pure water and aqueous dextran solutions containing various molecular weight hydrophilic dextrans. The rejections of the membranes were also determined with aqueous dextran mixtures using both a stirred dead-end ultrafiltration cell and a cross-flow cell. Progress in each project task is reported below.

Task 1. Prepare Poly(vinylidene fluoride)/Polyamide-Polyether Block Copolymer Nanofiltration Membranes

The nonporous nanofiltration membranes, consisting of a microporous poly(vinylidene fluoride) [PVDF] support membrane coated with a selective polyamide-polyether block copolymer layer, were prepared on our 12-inch wide continuous coating equipment, shown in Figure 1. The support membrane was fed from the roll through a dip-coating station, the drying oven, and was finally wound up on a product roll.

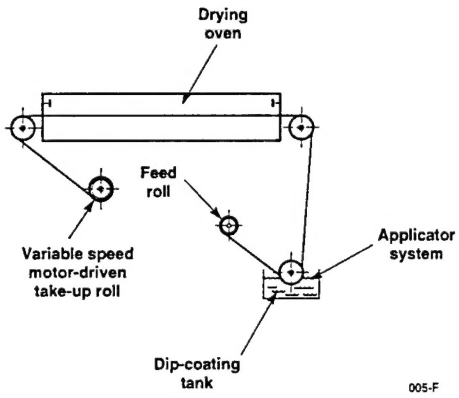

Figure 1. Schematic diagram of the MTR thin-film dip-coating machine.

Membrane samples were prepared from five different grades of Pebax: Pebax 1074, Pebax 4011, Pebax 3000, Pebax 1041, and Pebax 2533. The thicknesses of the Pebax layers were estimated from the known carbon dioxide permeability coefficients of the Pebax polymer grades and the pressure-normalized carbon dioxide fluxes of the composite membranes. The thicknesses of the Pebax layers ranged from 0.6 to 2.4 μm.

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Task 2. Determine Flux and Rejection of Nonporous Membranes and of a Conventional Porous Nanofiltration Membrane

Permeation experiments were performed with samples of the five types of Pebax composite membranes using pure water and aqueous solutions containing hydrophilic dextrans of various molecular weights . The initial concentrations of the dextrans in the aqueous solutions were about 1,000 ppm. The experiments were performed with both a stirred dead-end ultrafiltration system and a cross-flow system at room temperature, a feed pressure of 50 psig, and atmospheric permeate pressure. The pressure-normalized water flux was calculated from the permeate volume as a function of time, membrane area, and feed pressure.

The stirred dead-end filtration system, shown in Figure 2, has a hold-up volume of about 60 ml and a membrane area of 12 cm^2. An electromagnetic bar is used to stir the solution; the stirring speed was 500 rpm in these experiments. The feed flow in dead-end filtration is perpendicular to the membrane surface, so that the retained particles accumulate and form a surface fouling layer. The thickness of the surface fouling layer increases with filtration time, resulting in a decreasing permeation rate and an increasing solute rejection.

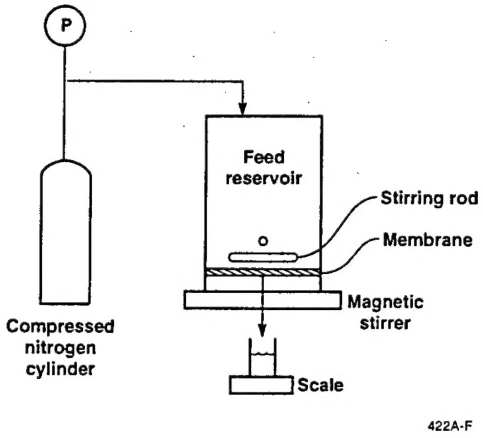

Figure 2. Schematic diagram of laboratory dead-end filtration system.

The cross-flow cell filtration system is shown schematically in Figure 3. The cross-flow cell has a membrane area of 20 cm^2 equipped with a small gear pump, a pressure gauge, and a flowmeter. The amount of liquid pumped into the cell can be adjusted manually to a feed pressure of 50 psig and a flow rate of 350 cm/min. The feed flow in the cross-flow filtration cell is along the membrane surface and the retentate returns to the feed tank, so that only small amount of the retained solutes can accumulate on the membrane surface during the filtration time.

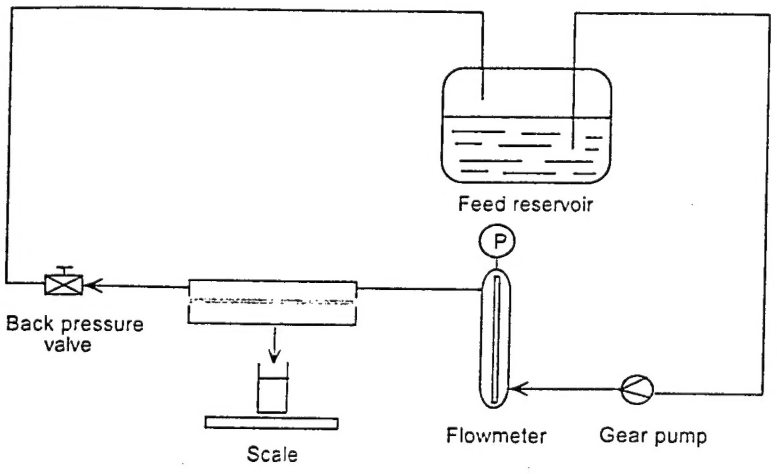

Figure 3. Schematic diagram of laboratory cross-flow filtration system.

Since the polyamide-polyether layer is smooth and nonporous, internal fouling cannot occur in these systems. In addition, surface fouling in the cross-flow system is expected to be less than in the stirred dead-end system.

The Pebax layer thicknesses and pressure-normalized water fluxes of the machine-made composite membranes in both systems are shown in Table 1. As expected, the pressure-normalized water fluxes of most Pebax membranes determined in the cross-flow filtration system were higher than those of the dead-end filtration because of less surface fouling. However, Pebax 4011 membrane had higher water flux (24 $L/m^2 \cdot h \cdot atm$) in the dead-end system than in the cross-flow system (15 $L/m^2 \cdot h \cdot atm$). This probably occurred because the thickness of the Pebax 4011 layer was uneven. Pebax solutions gel quickly at room temperature; therefore, the hot Pebax solutions used the dip-coating process may partially plug the pores of the PVDF support, resulting in an uneven Pebax layer. The water flux of the Pebax membranes also depends on the Pebax layer thickness.

Table 1. Pebax Layer Thickness and Water Flux of Pebax 4011, Pebax 1074, Pebax 3000, Pebax 1041, and Pebax 2533 Composite Membranes Using Dead-End and Cross-Flow Cells. Temperature: 23 °C; feed pressure: 50 psig; permeate pressure: atmospheric.

Membrane Type	Pebax Layer Thickness (μm)	Water Flux ($L/m^2 \cdot h \cdot atm$)	
		Dead-End Cell	Cross-Flow Cell
Pebax 4011	0.55	24	15
Pebax 1074	0.70	1.4	8.2
Pebax 3000	1.33	3.8	6.5
Pebax 1041	1.60	3.5	4.7
Pebax 2533	2.40	0.01	0.04

The pressure-normalized water fluxes of the nonporous Pebax composite membranes are shown as a function of water sorption of Pebax polymers in Figure 4. The water flux increases significantly with increasing water sorption of the polymers. The hydrophilicity of the various Pebax grades is indicated by the equilibrium water uptake (i.e. swelling of the polymer) during water permeation experiments. The hydrophilicity of Pebax polymers increases in the order: Pebax 2533, Pebax 1041, Pebax 3000, Pebax 1074, and Pebax 4011 and corresponds to the sorption of 1.2 wt%, 12 wt%, 28 wt%, 48 wt% and 120 wt% water, respectively.

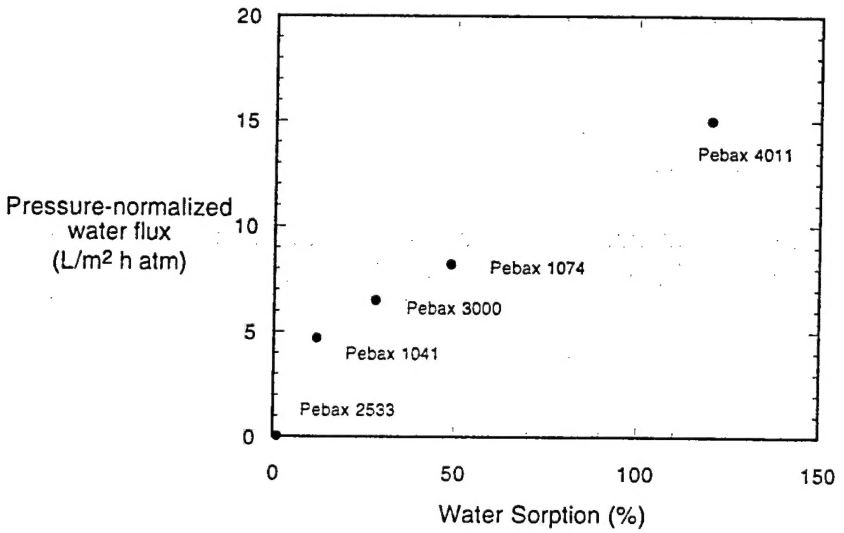

Figure 4. Pressure-normalized water fluxes of Pebax composite membranes in the cross-flow system as a function of water sorption of Pebax polymers. Feed temperature: 23 °C; feed pressure: 50 psig; permeate pressure: atmospheric.

Dextran Rejection

The rejections of the various nonporous Pebax composite membranes were determined with aqueous solutions of hydrophilic dextrans having molecular weights 1,200, 6,000 and 20,000 g/mol, respectively. Dextrans are highly hydrophilic polysaccharides. The compositions of the feed and permeate streams were analyzed with a total organic carbon analyzer (DC 190, Rosemount/Dohrmann, Santa Clara, California).

Rejection (R) is defined as:

$$R = (1 - c_p/c_f) \times 100\% \qquad (1)$$

where c_p is the concentration of the solute in the permeate solution and c_f is the concentration of the solute in the feed solution. If the membrane performs a complete separation (i.e. $c_p = 0$), the solute rejection is 100%. On the other hand, if the permeate solute concentration is equal to the feed solute concentration (i.e. $c_p = c_f$), the rejection is 0%.

The total fluxes of the aqueous dextran solutions and the rejections of the nonporous Pebax 4011, Pebax 1074, Pebax 3000 and Pebax 1041 composite membranes as a function of molecular weight of the dextran in the dead-end filtration mode and in the cross-flow mode are shown in Tables 2 and 3, respectively. The initial dextran feed concentration was about 1,000 ppm. The results in Tables 2 and 3 show that for a 6,000 g/mol dextran, Pebax 1074, Pebax 3000 and Pebax 1041 had a dextran rejection greater than 90% in dead-end mode and 78%, 80% and 90%, respectively, in cross-flow mode. For a 20,000 g/mol dextran, Pebax 1074, Pebax 3000 and Pebax 1041 had a dextran rejection of more than 90% in both systems. Thus, the molecular weight cut-off

of the nonporous Pebax membranes for hydrophilic dextrans is in the range 6,000-20,000 g/mol. In both systems, Pebax 4011 membrane showed lower dextran rejections than all other Pebax membranes. The molecular weight cut-off of the nonporous Pebax 4011 for hydrophilic dextrans is more than 20,000 g/mol. This is because Pebax 4011 is the most hydrophilic polymer; therefore, the interchain dimensions of the highly water-swollen Pebax membrane are large enough to allow passage of the hydrophilic dextrans.

Table 2. Total Fluxes and Dextran Rejections of Pebax Composite Membranes in Dead-End Filtration System. Feed solution: 1,000 ppm dextran; feed temperature: 23 °C; feed pressure: 50 psig; permeate pressure: atmospheric.

Pebax Type	1,200 g/mol Dextran		6,000 g/mol Dextran		20,000 g/mol Dextran	
	Total Flux ($L/m^2 \cdot h \cdot atm$)	Rejection (%)	Total Flux ($L/m^2 \cdot h \cdot atm$)	Rejection (%)	Total Flux ($L/m^2 \cdot h \cdot atm$)	Rejection (%)
4011					21	59
1074	1.0	86	1.2	98	1.1	99
3000	3.4	73	3.7	95	3.8	99
1041	3.5	70	3.6	94	3.6	98

Table 3. Total Fluxes and Dextran Rejections of Pebax Composite Membranes in Cross-Flow Filtration Cell. Feed solution: 1,000 ppm dextran; feed temperature: 23 °C; feed pressure: 50 psig; permeate pressure: atmospheric.

Pebax Type	1,200 g/mol Dextran		6,000 g/mol Dextran		20,000 g/mol Dextran	
	Total Flux ($L/m^2 \cdot h \cdot atm$)	Rejection (%)	Total Flux ($L/m^2 \cdot h \cdot atm$)	Rejection (%)	Total Flux ($L/m^2 \cdot h \cdot atm$)	Rejection (%)
4011					12	24
1074			8.2	78	5.4	96
3000	6.4	39	6.3	80	6.1	94
1041	4.5	57	4.4	90	4.4	96

Figure 5 shows the rejections of the nonporous Pebax 1074, Pebax 3000, and Pebax 1041 composite membranes in the cross-flow system as a function of water sorption of Pebax polymers. As expected, the rejection of the 6,000-g/mol dextran decreases significantly with increasing water sorption of the polymers. Swelling of the interchain dimensions of the polymer increases with increasing hydrophilicity and allows passage of the dextran.

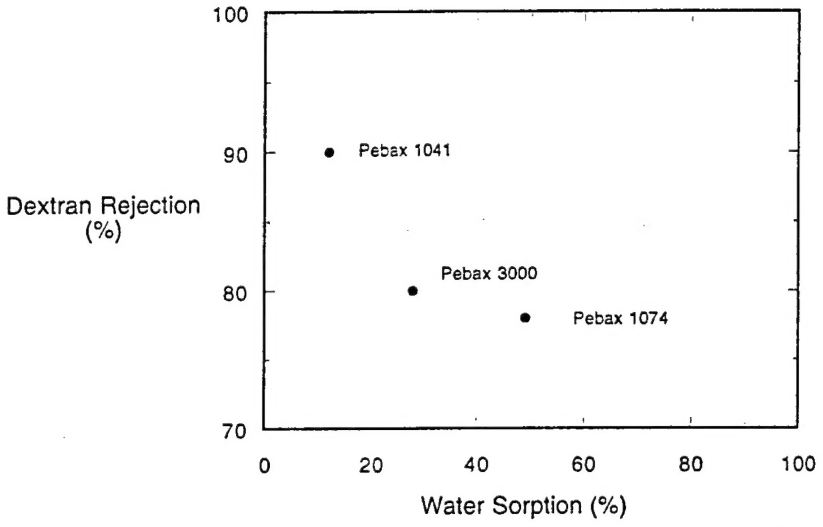

Figure 5. Rejection of Pebax composite membranes of 6,000 g/mol dextran in the cross-flow system as a function of water sorption of Pebax polymers. Feed temperature: 23 °C; feed pressure: 50 psig; permeate pressure: atmospheric.

Task 3. Prepare Laboratory-Scale Spiral-Wound Modules

No activity this period.

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Task 4. Determine Module Performance in Parametric Testing

No activity this period.

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Task 5. Manage Project and Prepare Reports

The second progress report on the project was prepared.

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4. PLANS FOR THE NEXT PERIOD

Next period, we will evaluate Pebax membranes with pure water and with various concentrations of aqueous emulsions containing soy bean oil and surfactant DC 193. We will determine the pressure-water normalized fluxes and rejections of Pebax membranes of oil/surfactant aqueous mixtures at a constant feed flow rate and various feed pressures and at a constant feed pressure and various feed flow rates. We will also prepare Pebax/PVDF composite membranes with two grades of Pebax 4011 and Pebax 1041. These Pebax membranes will be rolled into 2-inch-diameter spiral-wound modules that will be used in long term fouling experiments with pure water and with 1,000 ppm oil:surfactant DC193 aqueous mixtures.

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